

## Supporting Information for

### **Co-operation of Hydrogen Bonds and Dynamic Covalent Bonds Enables Energy-dissipative crosslinked Binder for Silicon-based Anodes**

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## **Experimental**

### **Synthesis of TCB binder film**

TCB binder aqueous solution was prepared through mixing and stirring tannic acid (TA, Shannxi herbchem biotech Co., Ltd), carboxymethyl cellulose (CMC, Guangdong Canrd New Energy Technology Co., Ltd) and boric acid (BA, Shanghai Macklin Biochemical Co., Ltd) with a mass ratio of TA: CMC: BA = 1: 1: 0.1. Firstly, TA (0.1 g) and CMC (0.1 g) were dissolved in deionized water. After stirring for 10 h, TA and CMC were dispersed homogeneously. Then, added a small amount of sodium hydroxide aqueous solution to adjust to weak alkalinity, that is, an environment suitable for borate bond formation. Finally, BA (0.01 g) was added into the solution with stirring for 0.5 h, and the TCB binder film was then generated after being dried in a vacuum oven at 70 °C for 24 h.

### **Preparation of electrodes and batteries assembly**

In the case of pure Si anodes, the weight ratio of silicon, conductive carbon black (CB, LITX200, Cabot), and binder was 7:2:1. In general, the mass loading of active material was kept at  $\sim 1.1 \text{ mg cm}^{-2}$ . For Si/C anodes, a weight proportion of 8:1:1 was applied for the electrode components including Si/C (950 mAh g<sup>-1</sup>), conductive CB, and binder, and the mass loading of Si/C active material was typically kept at  $\sim 2.5 \text{ mg cm}^{-2}$ .

The coin cells (CR2032) were assembled using Li metal and Celgard 2500 as the counter electrode and the separator, respectively. The electrolyte included 10 vol% fluoroethylene carbonates and contained 1.0 M LiPF<sub>6</sub> in ethylene carbonate and diethyl carbonate in a volume ratio of 1:1. The Si/C||LiFePO<sub>4</sub> full-cells were generated utilizing LiFePO<sub>4</sub> as the cathode. The above operation was assembled in the glove box.

### **Characterizations**

Fourier transform infrared spectroscopy (FTIR, Thermo Fisher Scientific Nicolet iS50) characterization was conducted for structure analysis. The surface composition of the initial Si particles and the cycled electrodes was explored through X-ray photoelectron spectroscopy (XPS, AXIS UltraDLD). The morphologies of electrodes were observed through field emission scanning electron microscopy (SEM, JSM-7600 Fs) and high-resolution transmission electron microscope (TEM, JEM2100). With a pulling rate of

5 mm per minute, 180° peeling tests were carried out on the universal testing system (UTM6503) to analyze the adhesive strength of electrodes containing different binders. The electrode sample was a long stripe shape with a width of 1 cm. The stripped tapes were observed through the optical microscope. The apparent viscosity of the slurry was measured by Rheogoniometer (MAS60). The following formula was used to determine the binders' swelling ratios (SR) in the electrolyte.

$$SR = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

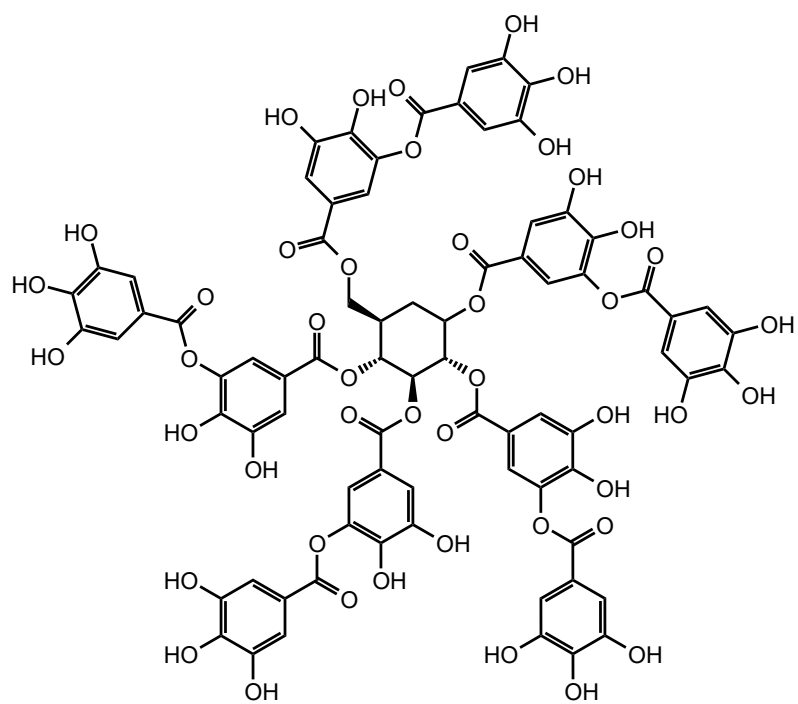
Where  $m_0$  refers to the original weight, and  $m_1$  refers to the weight of the binder immersed in electrolyte.

### **Electrochemical measurements**

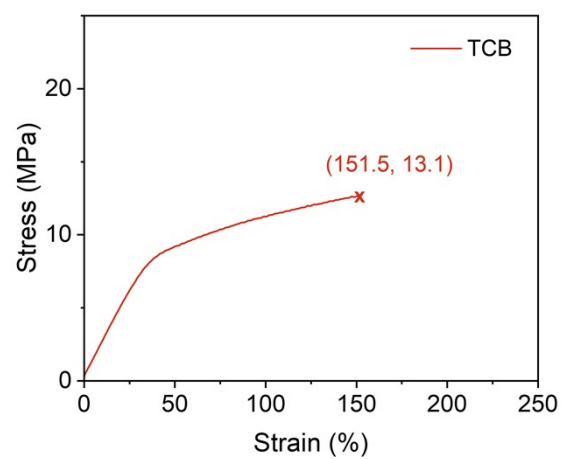
On a Land tester (CT2001A), galvanostatic charge/discharge tests were carried out with cut-off voltage intervals of 0.01 - 1.2 V for pure Si anodes, 0.01 - 1.5 V for Si/C anodes, and 2.5 - 4.0 V for Si/C||LiFePO<sub>4</sub> full-cells. The electrochemical workstation (Corrtest CS310H) was employed to conduct experiments on cyclic voltammetry (CV) and electrochemical impedance spectra (EIS). For EIS tests, an amplitude of 5 mV and a frequency interval of 10<sup>5</sup> to 0.1 Hz were employed. For CV tests, the voltage interval used to characterize the Si anode is 0.01 - 2.0 V.

### **Simulation**

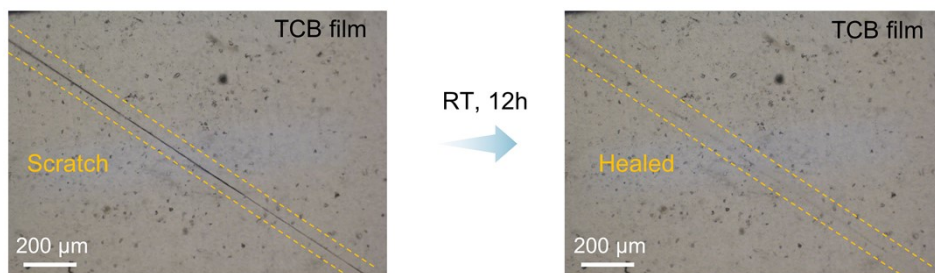
The Gaussian 09 suite of programs was used throughout to optimize and calculate hydrogen bond types and hydrogen bond energies. The B3LYP density functional method with the D3(BJ) dispersion correction was employed in this work to carry out all the computations. The 6-31G(d) basis set was used for the atoms in geometry optimizations using the PCM model with water as the solvent. Vibrational frequency analyses at the same level of theory were performed to characterize stationary points as local minima without any imaginary frequencies. The single-point energy calculations were carried out using the def2-TZVP basis set to provide better energy correction.



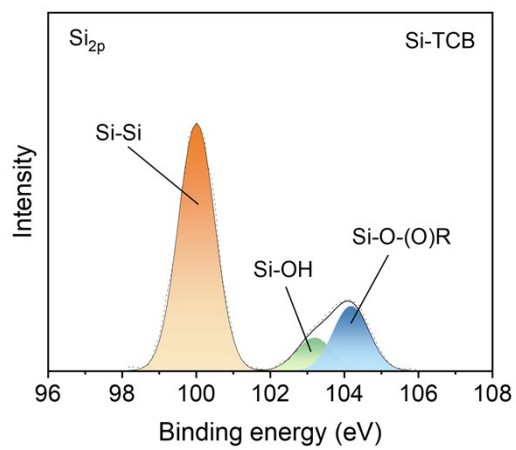
**Fig. S1.** Structure of TA.



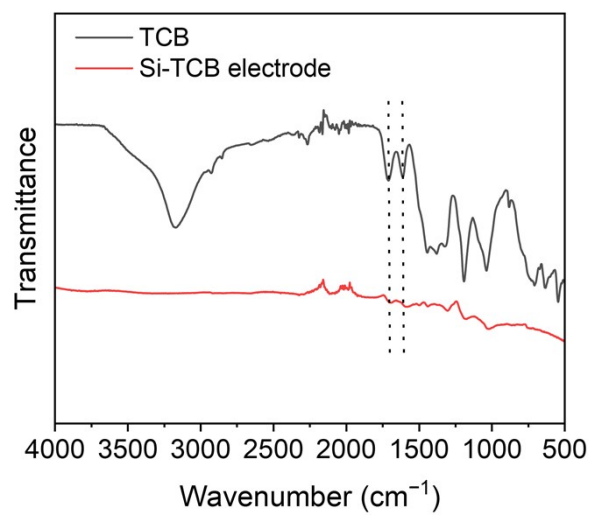
**Fig. S2.** Stress-strain curve of TCB film.



**Fig. S3.** Digital graphs of TCB film before and after self-healing.

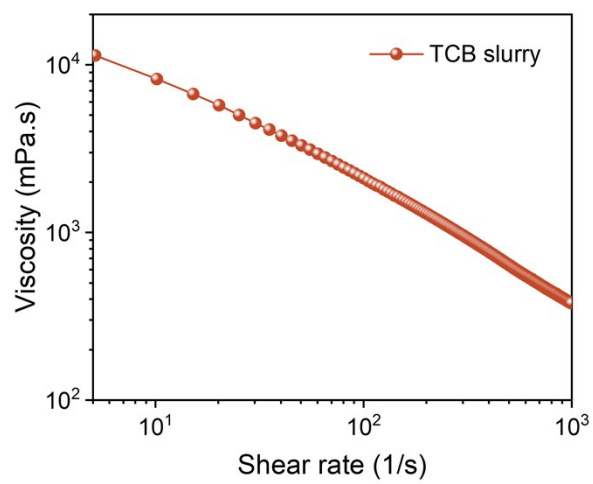


**Fig. S4.** XPS spectrum of Si-TCB anode.

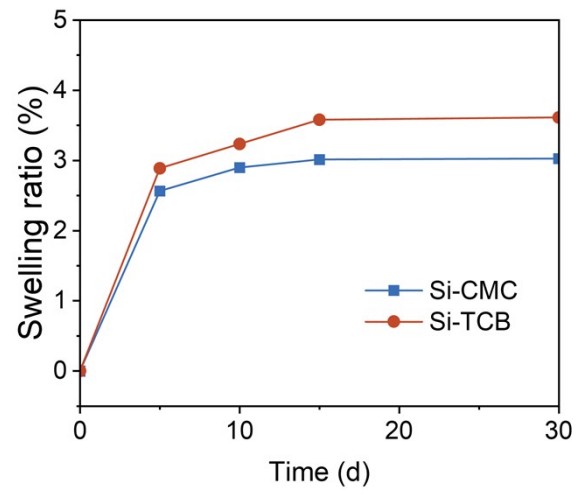


**Fig. S5.** FT-IR characterization on Si-TCB electrode.

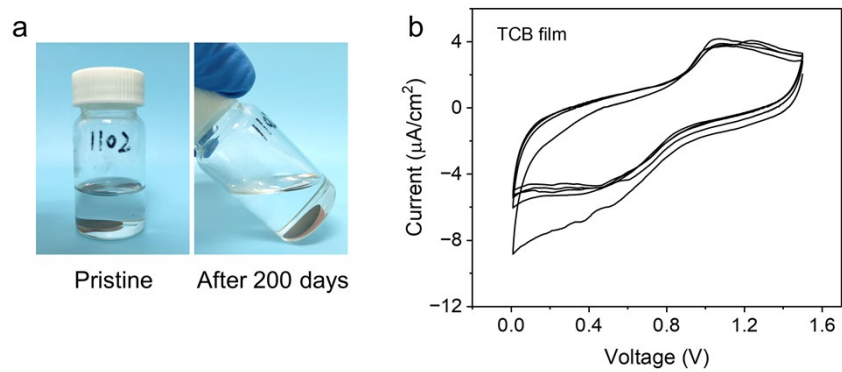




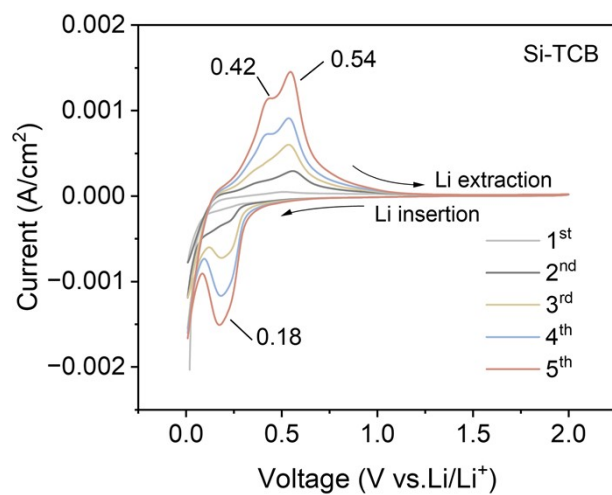
**Fig. S6.** Apparent viscosity of Si-TCB slurry.



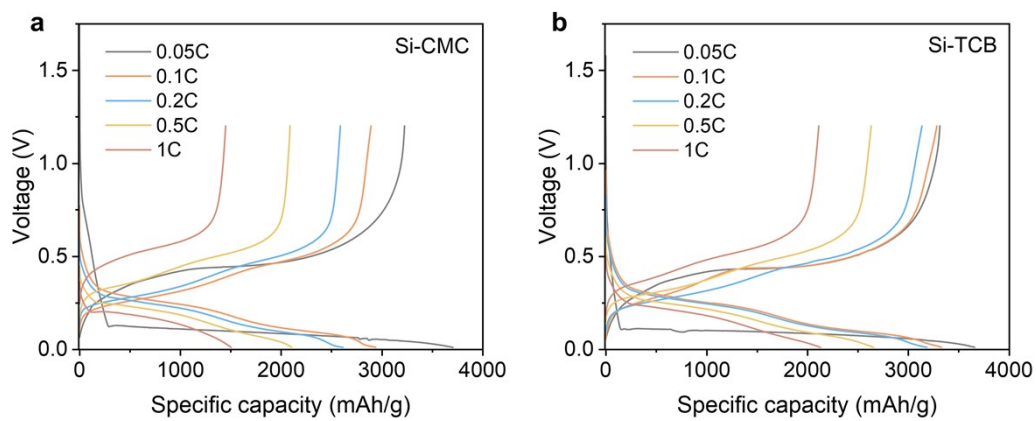
**Fig. S7.** The swelling ratios of different binders in the electrolyte.



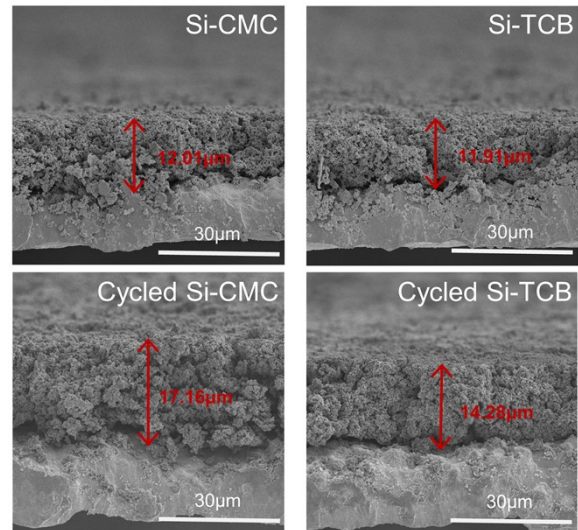
**Fig. S8.** (a) Photographs of Si-TCB electrode before and after being immersed in electrolyte. (b) CV curves of TCB film at 0.2 mV/s.



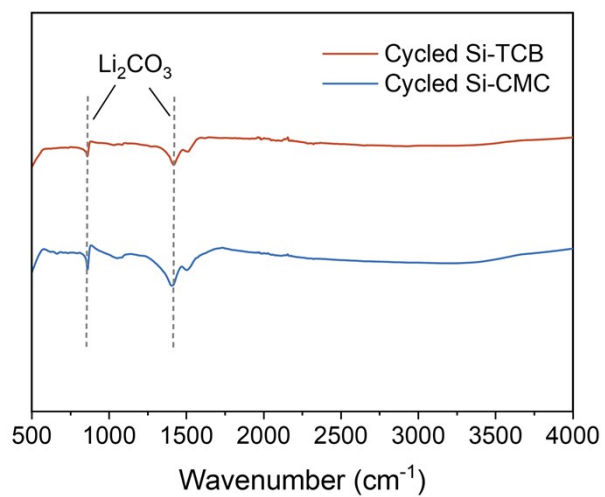
**Fig. S9.** CV curve of Si-TCB at 0.2 mV/s.



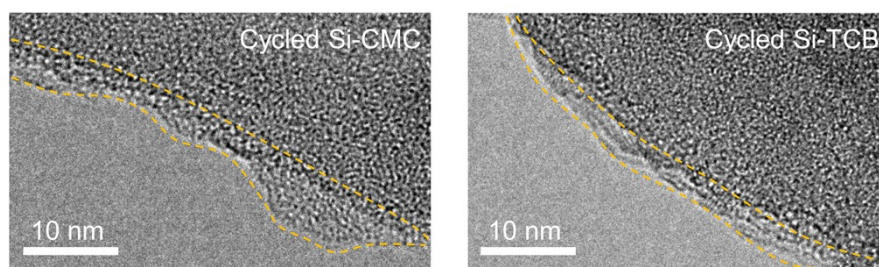
**Fig. S10.** Charge/discharge curves of (a) Si-CMC and (b) Si-TCB electrodes at different C-rates.



**Fig. S11.** Cross-sectional SEM images of Si-CMC and Si-TCB electrodes before and after cycles.

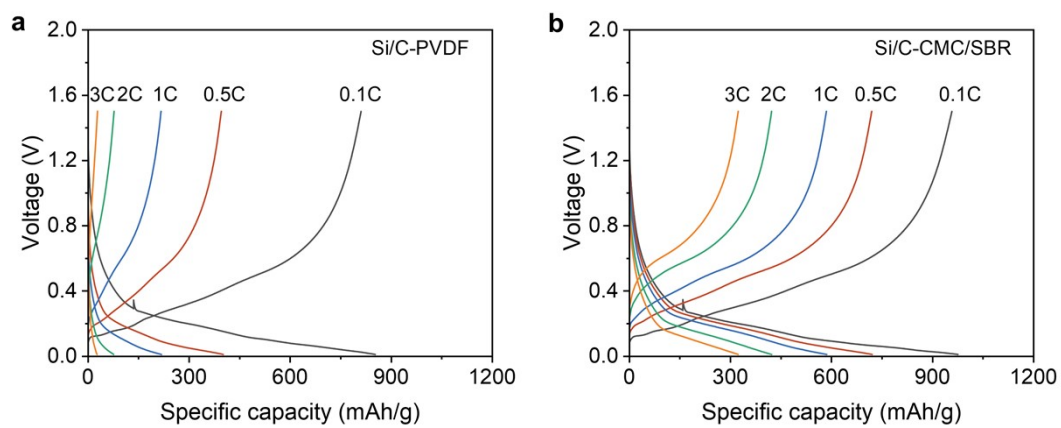


**Fig. S12.** FT-IR spectrum of Si-CMC and Si-TCB electrodes after rate cycles.

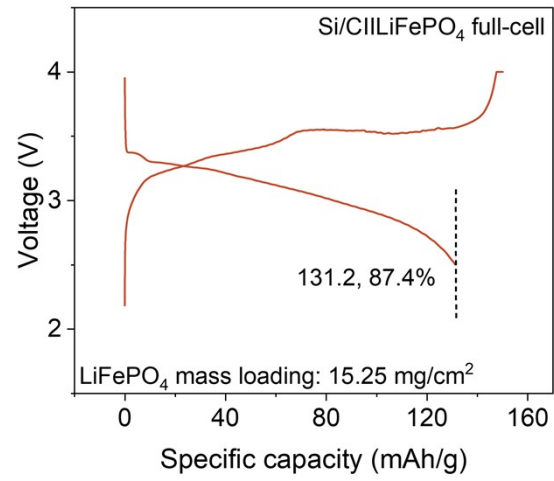


**Fig. S13.** TEM images of Si-CMC and Si-TCB electrodes after rate cycles.





**Fig. S14.** Charge/discharge curves of Si/C-PVDF and Si/C-CMC/SBR electrodes at different C-rates.



**Fig. S15.** Initial charge/discharge curves of Si/C||LiFePO<sub>4</sub> full-cell incorporating TCB as anode binder.